I. A NEW TYPE OF COUPLING REACTION 4, 4′-DIAROYLBIPHENYLS

II. 1, 4 ADDITION OF THE GRIGNARD REAGENT TO MESITYL ARYL KETONES

BY

MARVIN DOUGLAS ARMSTRONG

B.S., University of South Carolina, 1938

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SUBMITTED IN PARTIAL FULFILLMENT OF THE REQUIREMENTS FOR THE DEGREE OF DOCTOR OF PHILOSOPHY IN CHEMISTRY IN THE GRADUATE SCHOOL OF THE UNIVERSITY OF ILLINOIS, 1941

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I. A NEW TYPE OF COUPLING REACTION 4,4′ DIAROYLBIPHENYLS

Introduction

In a study of the action of the binary mixture, magnesium and magnesium iodide, upon halogen substituted benzophenones, Gomberg and Bailar found that *o*-bromobenzophenone did not undergo the expected pinacol reduction, but suffered a complete removal of the halogen from the aromatic nucleus.[1] They suggested that the steric hindrance of the halogen atom prevented coupling. This view was supported by the fact that *m*-and *p*-bromobenzophenones both coupled normally when treated with the binary mixture.

The present problem involved the preparation of several hindered halophenyl ketones and the study of their reaction with the binary mixture.

Experimental

p-Bromo- and *p*-chlorobenzoylmesitylene were coupled by magnesious iodide or any mixture of reagents capable of yielding it to form 4,4′-dimesitoylbiphenyl. The reaction proceeded readily to give a deep red precipitate, which hydrolyzed and formed a red solution in ether. This red compound was stable in the absence of oxygen, but was rapidly decolorized by oxygen to yield the product, 4,4′-dimesitoylbiphenyl. The reaction proceeds with an initial attack on the carbonyl group, and is not an ordinary Würtz-Fittig coupling brought about by the magnesium present. *p*-Bromobenzoyltriethylbenzene and *p*-bromobenzoyltriisopropylbenzene underwent the coupling readily.

m-Bromobenzoylmesitylene reacted with magnesious iodide to form a complex that reverted to the starting material when treated with water.

o-Bromobenzoylmesitylene reacted with the binary mix-

ture to form an intensely colored solution. Benzoylmesitylene was the only product that could be obtained from this reaction and no starting material could be recovered. All attempts to show the presence of an intermediate Grignard reagent were unsuccessful.

Summary

The reaction of the binary mixture, magnesium and magnesium iodide, with hindered halophenyl ketones has been studied. Hindered *p*-halophenyl ketones are coupled to the corresponding 4,4′-diaroylbiphenyls, *o*-halophenyl ketones suffer a reduction of the halogen atom, and *m*-halophenyl ketones are essentially unchanged by the reagent.

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II. 1,4 ADDITION OF THE GRIGNARD REAGENT TO MESITYL ARYL KETONES

Introduction

The first recorded instance of the addition of a Grignard reagent involving an aromatic nucleus is the reaction of phenylmagnesium bromide with benzophenone-anil.[1] The addition is made under forcing conditions and the product is *o*-phenylbenzohydrylaniline, which results from the rearrangement of the product formed by 1,4 addition of the Grignard reagent to the anil. Kohler and Nygaard[2] found that phenylmagnesium bromide would not add to diphenylbenzalacetophenone under ordinary conditions, but when the reaction was forced, a 1,4 addition which involved the benzene ring occurred. They isolated the enol-peroxide of the resulting enol and conclusively proved its structure.

Experimental and Discussion

Three mesityl aryl ketones were prepared and were caused

to react with the Grignard reagent. In most cases the reaction proceeded well in ethyl ether, but better yields were obtained by adding benzene and refluxing the solution at a higher temperature. The crude products in all cases were oils and considerable difficulty was encountered in obtaining crystalline compounds.

The reaction of phenylmagnesium bromide with *p*-bromobenzoylmesitylene consistently yielded more than 40 per cent of the expected amount of a compound which was shown to be a dihydroaromatic ketone. This substance was formed by ketonization of the enol obtained by the 1,4 addition of the reagent. None of the corresponding aromatic ketone, 2-mesitoyl-5-bromobiphenyl, was ever isolated. The addition of α-naphthylmagnesium bromide to *p*-bromobenzoylmesitylene yielded two isomeric dihydroaromatic ketones.

Phenylmagnesium bromide added to α-mesitoylnaphthalene in the same manner. The products were mesitoic acid and 2-phenyl-1-naphthol. They resulted from the oxidation of the enol formed by hydrolysis of the metallo-organic complex. Fuson and Kaiser[3] obtained a similar result by the addition of phenylmagnesium bromide to 2-mesitoylbenzofuran, isolating mesitoic acid and 3-phenylcoumaranone.

The reaction between phenylmagnesium bromide and benzoylmesitylene yielded *o*-phenylbenzoylmesitylene, which is formed by a 1,4 dehydrogenation[4] of the resulting enol. A considerable amount of an oil which had the properties of the expected dihydroaromatic ketone corresponding to *o*-phenylbenzoylmesitylene was also obtained, but it could not be purified. A small amount of another oxidation product of the enol was obtained. It possessed an empirical formula, $C_{22}H_{22}O_2$, but its structure was not shown.

Methylmagnesium iodide was found to add to benzoylmesitylene in a normal manner and yielded 1-mesityl-1-phenylethylene. The identity of the product was shown by comparing it with the compound formed by the addition of mesitylmagnesium bromide to acetophenone. This reaction was very un-

expected, as it is the only case in which a Grignard reagent has ever been shown to add 1,2 to a mesityl ketone.

Summary

Phenylmagnesium bromide was found to react readily with three different mesityl aryl ketones. The products were those which could be formed from the enols resulting from a 1,4 addition of the reagent. Three reactions of the enols were demonstrated: ketonization, an oxidative cleavage, and a 1,4 dehydrogenation.

Methylmagnesium iodide added 1,2 to the carbonyl group of benzoylmesitylene to yield a product which was shown to be 1-mesityl-1-phenylethylene.

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3. Fuson and Kaiser, Unpublished work.
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VITA

The writer was born in Wilmington, North Carolina on April 15, 1918, and attended the public schools of that city until October, 1933. At that time he moved to Columbia, South Carolina, and was graduated from Columbia High School in June, 1934. He attended the University of South Carolina and received the degree of Bachelor of Science from that institution in 1938. The same year he entered the University of Illinois as a University Scholar, and received the degree of Master of Science in June, 1939. From 1939 until 1941 he held a University Fellowship in Chemistry.

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